PHYSICOCHEMICAL STUDY OF ABSORPTION OF CO_2 INTO ELECTRIC ARC FURNACE SLAG

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ABSTRACT

Increase in the CO_2 concentration in atmosphere due to the combustion of fossil fuels has caused serious global warming. In dealing with this issue, the absorption of CO_2 into EAF steelmaking slag was experimentally studied by the utilization of mechanical grinding method. The final objective of this research is to develop a new mineral carbonation process that has a high efficiency in the capture and storage of CO_2 with low energy consumption and at the same time has some value added features that leads to the feasibility of the overall carbonation system.

In the first stage of this study, the absorption behavior of CO_2 into metal powders and CaO contained material was studied by dry grinding in a centrifugal ball mill. It was found that CO_2 was not decomposed during the grinding, but the sorption of it occurred on the ground sample. In both cases of CaO and waste concrete, formation of $CaCO_3$ was confirmed. While, in the case of metal powders, the CO_2 absorption into ground powders was firstly occurred, thereafter, it decomposed to form metal oxides and carbon. CO_2 sorption into the samples depended on the newly exposed surface area that was formed by grinding. It was found that the newly exposed surface area increased linearly with the increase in the grinding time. However, the dry grinding resulted to the agglomeration of particles in the latter stage of grinding. The agglomeration of particles has then led to the limitation of the CO_2 absorption.

In the next stage, the behavior of CO_2 absorption into EAF normal and stainless steel reducing slag was investigated with wet grinding method. The slag was wet ground under CO_2 atmosphere by a vibrating ball mill which has larger capacity than the centrifugal ball mill. The amount and the initial rate of CO_2 absorption for the wet grinding were higher than those for the dry grinding. The optimum ratio of fillings to vessel's volume was found to be about 1/2. CO_2 was stored into the slag mainly as $CaCO_3$ and no desorption of CO_2 was observed. Thus, this indicates that the CO_2 can be stored permanently inside the slag with this method. This study also revealed that the increase in the interfacial area between CO_2 and the slurry of water and slag was necessary to enhance CO_2 absorption. It was found that the absorption capacity of CO_2 into the normal and stainless steel reducing slag using this method on the most optimum grinding condition was 0.21 and 0.31 kg CO_2/kg slag respectively.

To profoundly investigate the mechanism of CO_2 absorption, study on the absorption behavior of CO_2 into EAF normal and stainless steel oxidizing slag with wet grinding method

was also conducted. The results showed that the conversion ratio of CaO to $CaCO_3$ was not solely affected by the CaO content in the slag, but by the CaO/Al_2O_3 ratio in the slag. The conversion ratio linearly increased with the increase in the CaO/Al_2O_3 ratio. The rate of CO_2 absorption in the slag with wet grinding method was highly depended on the dissolution behavior of Ca^{2+} ion from the slag into water and the interfacial area between the CO_2 gas and water. The rate increased with the increase in the both factors. The dissolution behavior of Ca^{2+} differed between each slags depended on the main phases reaction in the slag. Thus, the main phases in each slags affected the overall reaction of the CO_2 absorption. The $2CaO \cdot Al_2O_3 \cdot SiO_2$ was found to hinder the absorption of CO_2 into the slag. While $CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ phases in the slag were favorable for the CO_2 absorption. It was found that the absorption quantity of CO_2 into the stainless steel oxidizing slag with low Al_2O_3 content on the most optimum grinding condition was about 0.26 kg CO_2/kg slag. Comparison between the amount of CO_2 absorption in this study and the amount of CO_2 emitted from various power plants, which was estimated by the energy consumption of the vibrating mill, revealed that the former was not always higher than the latter. Reduction amount of 1% from overall CO_2 emission from steel industry can be expected by this method. Use of other possible materials will lead to the increase in the potential reduction amount.

The overall cost for the system is expected to be very low and this also indicates that this method is economically feasible. Along with the absorption of CO_2, Zn could be removed by using this method with high removal ratio. The dissolutions of Cr were low for all conditions and the pH of the slurry were within the environmental quality standard. It was also found that even though the mortar made from the ground carbonated slag can't be used to concrete, however, it can still be used as normal mortar.

CONTENTS

CHAPTER 1.

INTRODUCTION

1.1 Background – Emissions of CO_2 Gas

Long before the Industrial Revolution in the late of 18th century, human beings had only a moderate need for energy. They mostly relied on the energy and strength from human or brute animal to do work, and relied on the natural sources like wind to move something [1, 2]. To keep on living, human beings and all other living creatures require energy in the form of food and heat which were usually supplied by food, and sometimes by sunlight, wind, hot water etc). We also use energy for a number of other purposes, such as clothing, shelter, transportation, entertainment, cooling and the construction of tools [3].

Rapid growth in industrialization began in the late 18th century, and this period was often considered as the start of the Industrial Revolution. By the beginning of the 19th century, inventions were not just limited to the cotton industry. Steam engines were invented, providing a faster mode of transportation, and this has resulted in reduction of the uses of horses and carriages. Steam engines and other machinery, of course, required coal as fuel source and this has released the first emissions of carbon dioxide (CO_2) and other gases which has then led to the increase in the concentration of the greenhouse gas (GHG) in the atmosphere and declining of air quality in many cities [4].

High energy consumption during the industrial revolution has brought the human race comfortable life. On the other side, as stated above, the combustion of a large amount of fossil fuels also led to the tremendous amount of CO_2 gas emission which is one of the green house gases. According to the report by the Intergovernmental Panel on Climate Change (IPCC), the global atmospheric concentration of CO_2 has increased from a preindustrial value of about 280 ppm to 379 ppm in 2005. The annual growth rate of the CO_2 concentration during the last 10 years (1995–2005 average: 1.9 ppm per year) is larger than that from the beginning of continuous direct atmospheric measurements (1960–2005 average: 1.4 ppm per year) [5]. Fig. 1-1 shows the amount of CO_2 gas emission in the world from year 1980 to year 2008, based on the report from Energy Information Administration (EIA) United States [6]. The amount of CO_2 gas emission is increasing year by year. It increased from about 18.5 billion tons in 1980 up to 31.5 billion tons in 2008. The amount of CO_2 emission in 2008 increased about 45% in comparison to that in 1990 which is the benchmark year under the Kyoto Protocol [7].

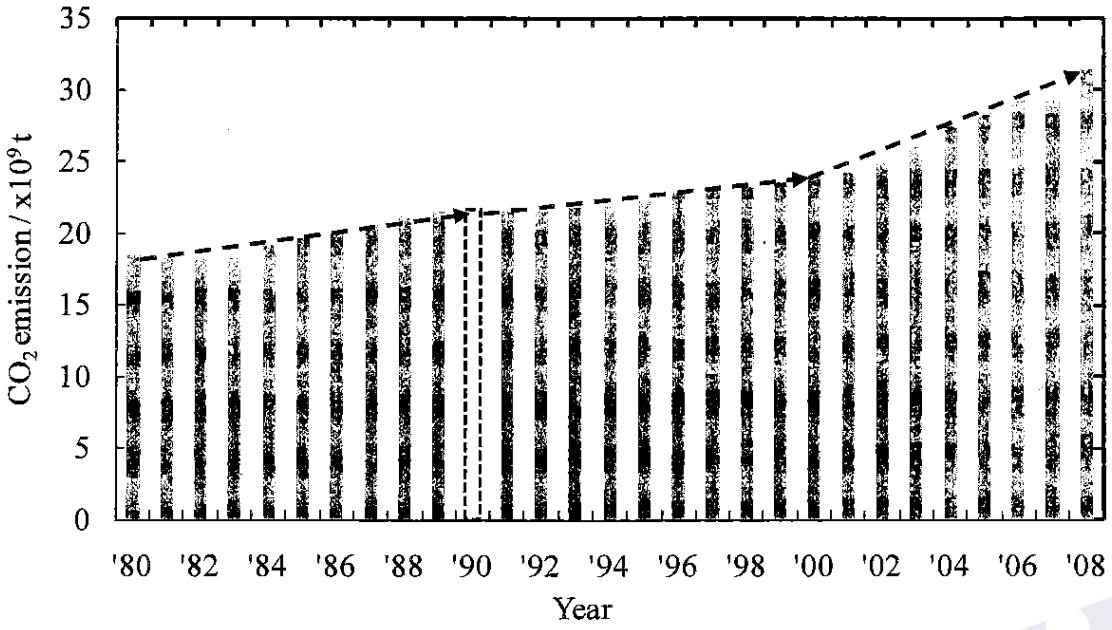


Fig. 1-1 Trend of carbon dioxide emission in the world, 1980 – 2008.

Table 1-1 Distribution of carbon on earth [13]

Source	Amount [$\times 10^{15}$ kg]	Relative amount [%]
Calcium carbonate	35,000	46.64
Ca-Mg-carbonate	25,000	33.31
Total carbonates	60,000	79.99
Sedimentary carbon (e.g. graphite)	15,000	19.99
Fossil fuels	4	0.0053
Other geological carbon	15,004	19.99
Total carbon in lithosphere ('dead' carbon)	75,004	99.94
Oceanic HCO_3^- and CO_3^{2-}	42	0.056
Dead surficial carbon (e.g. humus)	3	0.0040
Atmospheric CO_2	0.72	0.00095
All life	0.56	0.00074
Total non-geological carbon ('live' carbon)	46.28	0.06

The concentration of CO_2 in the atmosphere is modulated by numerous processes collectively known as the "carbon cycle". The "carbon cycle" is dominated by natural processes such as rock weathering, plant photosynthesis, soil carbon stocks and ocean sinks [8-12]. Over geological times, rock weathering process that occurred naturally is an important carbon sink. The carbonate rocks form the world's biggest carbon reservoir as shown in Table

1-1 [13]. However, it is estimated that the natural processes can only absorb about half of the amount of CO_2 gas emission, so there is a net increase of about more than 10 billion tones of atmospheric CO_2 per year [14-16]. This positive imbalance between the emission and the absorption results in the continuous increase in the atmospheric concentrations of CO_2 gas.

There are several sources of the CO_2 gas emission [17-24]. Based on the World Resources Institute (WRI) United States, the energy use is the major source for the production of GHGs with the electrical power generation, transportation and the industrial sectors are the major contributors for the CO_2 gas emissions [24]. This fact is also in line with the report announced by IPCC on the sources of CO_2 emissions from fossil fuel combustion in 2005. The report stated that the power generation, transportation and industrial sectors dominating the current global CO_2 emissions, accounting for more than 80% of total CO_2 emissions [18].

Due to the annual uptrend tendency of CO_2 gas emissions as shown in Fig. 1-1, United Nations Framework Convention on Climate Change (UNFCCC or FCCC) was founded at the United Nations Conference on Environment and Development (UNCED), informally known as the Earth Summit, in June 1992 [25]. The UNFCC has adopted the Kyoto Protocol in order to reduce the CO_2 gas emission into atmosphere on 11th December 1997 in Kyoto, Japan and this protocol came into force after Russia ratified it in February 2005 [26]. The protocol aims to decrease GHG emissions on average of 5.2% against the level of 1990, between 2008-2012.

Japan was the host for the UNFCC meeting in 1997 that has led to the adoption of Kyoto Protocol. Based on the data by EIA [6], Japan ranked fifth in the list of CO_2 gas emission by all country in the world after China, United States, Russia and India. Meanwhile, based on National Greenhouse Gas Inventory Report of Japan by the Ministry of the Environment in Japan [23], in 2008, the total amount of CO_2 emission was approximately 1.22 billion tons as shown in Fig. 1-2. Even though it showed slight decrease in comparison with that in the previous year, however, this amount was 6.3% higher than that in 1990. The breakdown of the CO_2 emission by major sources shown in Fig. 1-3 revealed that the CO_2 emission from the industries including steelmaking, manufacturing, fishery and so on was the major contributor of CO_2 emission and it accounted for 34.4% of the overall amount of CO_2 gas emitted in 2008. Other main contributors were the transportation sector that also contributed to the 19.3% CO_2 emission and the commercial sector with 19.0% contribution. These proportions were only originated from the combustion of fuel to generate energy for these sectors. Out of the proportion by the industries, about 15% or 176 million tons of CO_2 gas was contributed by the steel industry [27]. Therefore, in order to reduce the emission of CO_2, Japanese steelmakers

have established the Voluntary Action Program for Environmental Protection by Steelmakers in December 1996 [28]. Based on this action, the steel industry has decided to reduce its energy consumption by 10 % of the level from 1990 to 2010. For example, JFE has made a lot of effort in reducing the CO_2 emission from their steelmaking processes. The company invested 100 billion yen (USD$1.12b) from April 2006 till March 2009 for the CO_2 reduction projects such as development of Super-SINTER^{TM} (Secondary-fuel Injection Technology for Energy Reduction) technology for the injection of hydrogen-based fuel into a sintering furnace and makes the sintering process more energy efficient, and finally lead to the reduction of CO_2 emissions. It was estimated that about 60 thousand tons of CO_2 emission could be reduced yearly by this technology [29].

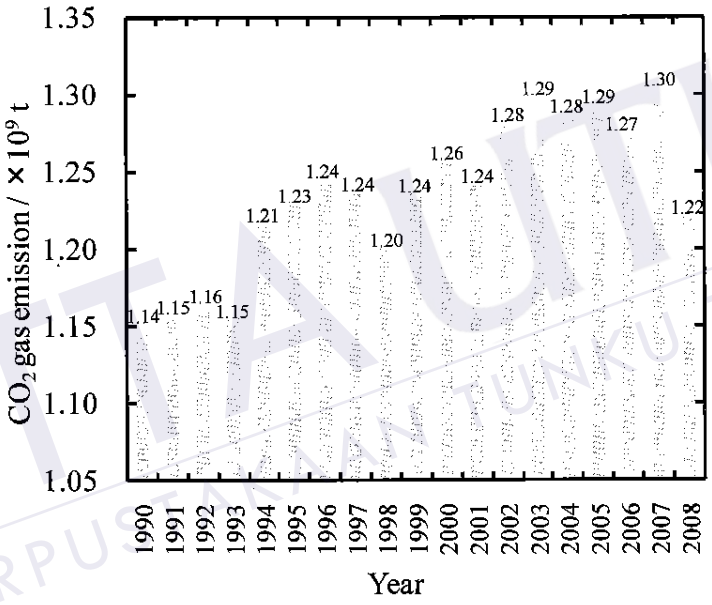


Fig. 1-2 Overall trends of CO_2 gas emission in Japan from 1990 to 2008.

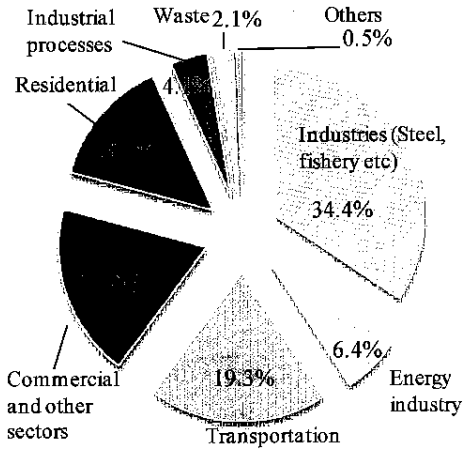


Fig. 1-3 Contributions of CO_2 gas emission by sources in Japan during 2008.

1.2 Greenhouse Gas Effect - Climate Change and Global Warming

A greenhouse gas which is a gas in atmosphere, absorbs and emits radiation within the thermal infrared range. This radiation absorption and emission process is the fundamental cause of the greenhouse effect [30]. The basic mechanism of the "effect" is as illustrated in Fig. 1-4 [5]. The Earth receives energy from the Sun in the form of visible light. This light is absorbed at the Earth's surface, and re-radiated as thermal radiation. Some of this thermal radiation is absorbed by the atmosphere and being released to the outer space, and some is re-radiated back towards the Earth and absorbed by the Earth's surface. Thus the presence of the atmosphere results in the surface receiving more radiation than it would when the atmosphere absent; and it is thus warmer than it would be [31]. This natural phenomenon of greenhouse effect keeps the Earth at the suitable temperature. However, this natural greenhouse effect is currently being disrupted through the human activity by the enormous release of additional anthropogenic greenhouse gases, especially CO_2 into the atmosphere.

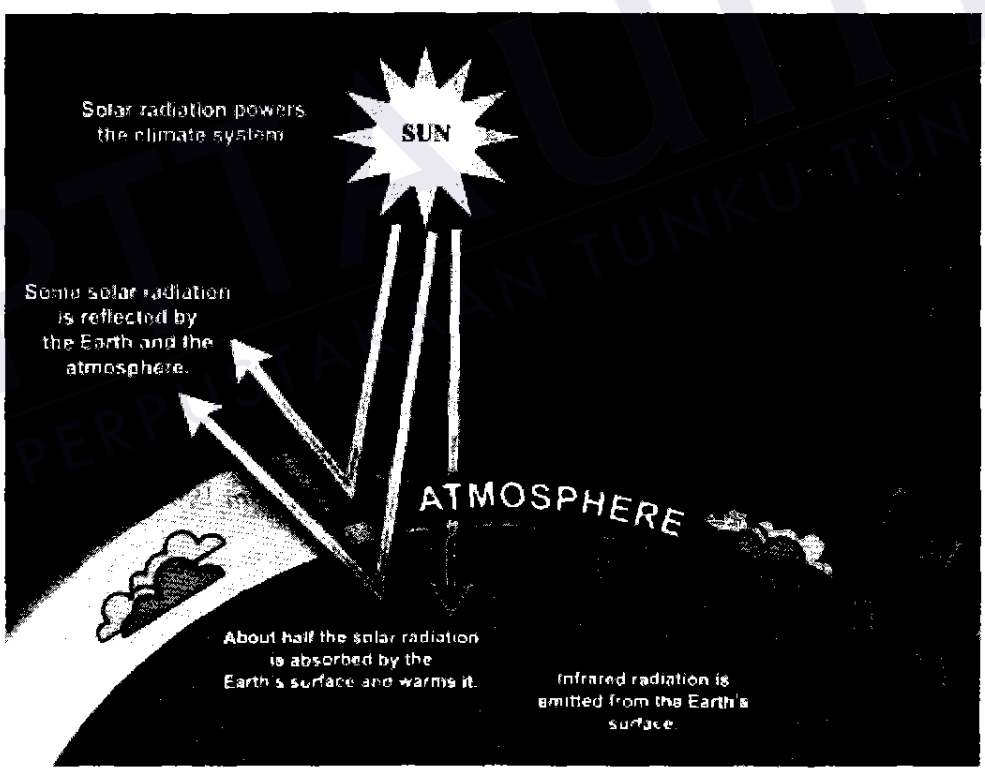


Fig. 1-4 An idealized model of the natural greenhouse gas effect [5].

The release of the CO_2 into the atmosphere, which also means the increase in the CO_2 concentration in the atmosphere, has brought serious effects on climate change and global warming [32-36]. Each country is naturally concerned with the potential damage that may

arise from climate change over the coming decades because it will affect domestic and international policies, trading patterns, resources use, regional planning and the welfare of people [37-41].

Global climate change will be remaining as one of the biggest environmental threats over the coming century. Although there are many uncertainties about how regional climate will change, the effects of climate changes are likely to be profound [42]. Several effects that have been brought by the climate change will be described below.

1.2.1 Increase in the average temperature of the Earth

According to the report by IPCC, 11 of the last 12 years (1995-2006) rank among the warmest years in the record of global surface temperature [43]. However, for about 100 years, since 1906 till 2005, the global temperature has increased approximately 0.74°C, and the rate of warming averaged over the last 50 years is nearly twice as large as that for the last 100 years [44].

1.2.2 Polar ice caps and sea ice melting

Satellite data from 1978 shows that average area of Arctic sea ice has shrunk by 2.7% per decade. Mountain glaciers and snow were found to be declined in both hemispheres [43, 45-47]. According to S.E. Stammerjohn et al., the Antarctic Peninsula region is undergoing rapid change which are; a warming in winter of almost 6°C since 1950, the loss of six ice shelves, the retreat of 87% of the marine glaciers, and the decreases in winter sea-ice duration [45].

1.2.3 Rising of sea level and flood

Global average sea level has risen since 1961 at an average rate of 1.8 mm/yr and since 1993 at 3.1 mm/yr due to the melting of glaciers, ice caps, and polar ice sheets [43]. Increasing floods at certain area in the world due to the global climate change was also reported [48].

1.2.4 Drought and heat waves

The impact of climate change on drought and heat waves has begun to be unpacked through the analysis of climate-related and biological feedback loops [49-52]. Over the past 50 years, cold days, cold nights and frosts have become less frequent on most land areas, whereas hot days and hot nights have become more frequent. Heat waves have become more

frequent and have been spreading over most land areas. Especially, Africa will receive the worst of it. According to the United Nation Environment Programme (UNEP), global warming will exacerbate the conditions of water supply and could lead to internal conflicts, regional unrest and war [53].

1.2.5 Volcanic explosions

Global warming could also indirectly lead to the occurrence of volcanic explosions. C. Pagli et al. have suggested that the global warming has also a profound effect on the melting of magma. As the ice disappears, it relieves the pressure exerted on the rocks deep under the ice sheet, and this could lead to the increase of the rock melting rate into magma. In Iceland there are several active volcanoes under the ice. The last big eruption was in 1996 at Gjàlp, and before that in 1938 - a time gap of 58 years. But Pagli et al. say that the extra magma produced by the melting of the ice cap could supply enough quantity of magma to cause similar eruptions every 30 years on average [54].

1.2.6 Acidification of sea water

The increasing rate of CO_2 concentration in atmosphere is predicted to result to the acidification of sea water [55-56]. F. Touratier et al. reported that since the year 2001, all waters (even the deepest) in the Mediterranean Sea region have been acidified by -0.14 to -0.05 pH unit since the beginning of the industrial era. This change of pH of seawater may affect a very large number of chemical and biological processes. It is predicted that a lot of ocean ecosystems such as bivalve shells, coral reefs, and so on, which are composed of calcium carbonate, will be highly affected by the acidified sea [57-60].

1.2.7 Cyclones and hurricanes

Several theories and models that have been made predict that the hurricane and cyclone intensity should increase with increasing global mean temperature [61-64]. T.R. Knutson et al. have found that the hurricanes that formed under warmer and high CO_2 conditions are more intense and frequent than under present conditions [62]. Similar report by K. Emanuel also stated that the intensity of hurricane power is highly correlated with the temperature of the sea surface. This is one of the climate signals that was brought by the global warming [65].

1.2.8 Health problems and spread of diseases

Climate change may affect health condition through a range of pathways, for example as a result of increasing frequency and intensity of heat waves. It may also changes the distribution of vector borne diseases and increases the risk of disasters and malnutrition [36, 66-67]. Moreover, some kind of diseases might be spread through various routes such as rodent, water, food and air [67]. When northern countries are warmed, diseases carried by insects will migrate north, and this may resulted to the infection of the diseases to human.

1.2.9 Desertification

Degradation of the land ecosystem commonly described as "desertification" progressed by various processes found to be occurred at many areas in the world [68-70]. According to the UNEP, all regions in which the ratio of total annual precipitation to potential evapotranspiration (P/ET) ranges from 0.05 to 0.65 should be considered vulnerable to desertification. Such regions occupy 40% of the global terrestrial area.

1.2.10 Economic consequences

Most of the effects of anthropogenic global warming won't be good. These effects spell economic consequences worldwidely. Hurricanes cause billions of dollars in damage, treatment and control of diseases require huge amount of money and any financial conflicts in handling budget for the mitigation of global warming might exacerbate all of the situations. Because this would be much affecting the decision that should be made by all country in the world, a lot of countries currently are really concern on a new economic growth path with low environmental impacts [71-72].

1.3 Production of Slag

The steel industry is one of the key industries in the world due to the high demand especially from building construction, automotive and machinery sectors. Based on the World Steel Association (WSA) report, the world crude steel production in 2008 was approximately 1326.5 million tons [73]. Along with the production of steel, the steel industry also generates steelmaking slag as a by-product. These slags can be broadly divided into blast furnace slag and steel slag. In the blast furnace (BF), constituents other than iron in the iron ore are melted and become slag together with the ash of coke, and the slag was separated from the pig iron and recovered. This BF slag has components similar to those of natural rocks, and about 290 kg is generated per ton of pig iron. On the other hand, the steelmaking process which consists

of refining pig iron, scrap and other material to produce steel leads to the production of steel slag. It can be divided into basic oxygen furnace (BOF) slag and electric arc furnace (EAF) slag with generation amounts of 110 and 120 kg per ton of crude steel respectively [74]. The EAF steel slag consisted of two different types of slag which are the oxidizing and reducing slags, with generation amounts of 70 and 50 kg per ton of crude steel respectively.

The BF slag composed of two types of slag; water granulated slag and air cooled slag. The water granulated slag is a sand-type slag, which is manufactured by spraying high-pressure water on molten blast-furnace slag. It is used as a cement material, material for civil engineering and construction, silicate-calcium fertilizer, and raw material for high-grade glass [75-76]. On the other hand, the air cooled slag is a lump produced from molten BF slag by air-cooling and appropriate water spraying. The product is then crushed and screened in accordance with the specified application and sold as materials for road base, rock fiber, concrete aggregates and cement clinker. Almost all of the BF slag has been used for the above purpose.

On the other hand, the steel slag has been used with air cooled BF slag in road building as a composite roadbed material [77]. It is also used as stabilizer and fertilizer of soil as well as materials in the cement production industry [78]. However, the steel slag must be aged naturally for 6 to 9 months at an outdoor yard to assure that it is stable and ready to be used. This is because of it's tendency to self-degradation. Usually, the steel slag contains free lime and the hydration ability of free lime can cause a volume expansion [79]. This problem has limited the utilization of the steel slag in the specified areas and thus, not all of the steel slag has been reused. For example, in Japan, about 14 million ton of steel slag was produced yearly in the basic oxygen furnace and electric arc furnace. About 439 thousand tons of steel slag was not reused and was sent to landfill for disposal in 2008 [80]. This problem had been worsen by the reduction of public work projects and, moreover, other recycled materials, such as reused roadbed materials and fly ash, become competitor of the slag in the fields [81-82]. Therefore, the amount of unused slag is expected to increase in the future unless a new re-utilization technology of slag is developed. It is always a big problem for the steel manufacturers to handle or dispose the unused slag. Previous efforts have focused on in-plant recycling of the by-products, but only limited success has been achieved. As a result, large amounts of various slags have been stockpiled at steel mills or disposed into landfills. After more than 50 years of stockpiling and landfilling, available mill spaces have been diminished and environmental constraints have been increased [83]. The disposal of slag to landfill was use to be the cheapest method, but cost of it is rising rapidly [84]. For instance, in the UK,

various regulations and rising taxes will soon make the disposal to landfill more expensive than the alternatives of reuse, recycle, etc. Furthermore, the remaining landfill areas can no longer accommodate all the dumped slag unless a new one built. Thus, there is a vital need for a new technology with less time, less money and energy consuming, low environmental impact and some added values. A lot of new technologies, techniques and inventions regarding to the recycling and utilization of the steel slag have been introduced in many fields [85-87]. Y. Kazuya et al. succeeded in the invention of new products as materials for improvement of coastline and coastal marine environments. They invented an environmental friendly block called "Ferroform" which is made mainly from slag and absolutely free from natural aggregate, and a large carbonated slag block called "Marine Block" which is made from steelmaking slag. The invention of these products has provided a more suitable environment for the growth of micro organisms than concrete because Fe, Si, and other elements essential for the growth of organisms are contained in steelmaking slag. Furthermore, a seaweed growth at the Marine Block was confirmed in the all marine areas and these might create an environment which is very similar to a natural shallows for diverse organisms [85]. In the other fields, utilization of steelmaking slag for the absorption of ammonium and phosphate ions from aqueous solution was studied by V.K. Jha et al. [86]. They have found that the slag-$Al(OH)_3$ mixture heated at 900°C has the highest PO_4^{3-} uptake capacity , while the slag-$Al(OH)_3$ mixture heated at 800°C has the highest uptake of NH_4^+.

Another utilization of steelmaking slag that has also received much attention in recent years is the carbonation process of the slag for the reduction of CO_2 gas in atmosphere [88-91]. Interest in using the steel slag as an absorbent of CO_2 has arisen because it is abundantly available, rich in metal oxide that favorable to the CO_2 absorption and most often produced near to the emission source of CO_2. A permanent and safe storage of CO_2 can also be expected from this process [88, 92]. Furthermore, the carbonation of the waste materials could reduce the harmful substances, namely heavy metals, because they would be either absorbed or insolubilised, or physically encapsulated [93].

1.4 Related Works of Technology on CO_2 Mitigation

Based on the UNFCC, the stabilization of CO_2 in the atmosphere can only be achieved when the rate of addition of CO_2 to the atmosphere equals the rate of removal of it from atmosphere. In other words, the rate of anthropogenic emissions must be balanced by the rate of uptake by natural processes such as absorption of it to the ocean and the biosphere [18]. However, as explained in 1.1, the natural processes can only absorb about half of the amount

of CO_2 gas emission. Consequently, there is a net increase of about more than 10 billion tones of atmospheric CO_2 per year [14-16]. Furthermore, in the current energy system, the combustion of the fossil fuels, namely, oil, coal and natural gas, supplies 85% of world energy demand [94]. These fuels will likely continue to be used in the next decades due to their low cost and high availability. Accordingly, the development of mitigation technologies for the anthropogenic CO_2 is urgently required to restraint the increase in atmospheric CO_2 concentration.

Various attempts and actions have been made to ameliorate global warming, such as the improvement of the energy efficiency or energy saving of existing processes, the use of less carbon-intensive fossil fuels, the utilization of low- or near-zero carbon energy sources, introduction of new policies and legislations, CO_2 capture and storage technology and so on [95-98]. These wide varieties of technologies would be a potential means to reduce net CO_2 emissions and/or atmospheric concentrations. However, the usability of each technique will be highly depended on factors such as cost, capacity, environmental impact, the rate at which the technology can be introduced, energy penalty and social factors such as public acceptance [18].

1.4.1 Energy efficiency and energy saving technology

Energy issues must be considered from three key factors; accessibility, availability and acceptability [99-100]. Accessibility is the provision of affordable modern energy services with low energy tariff. Availability covers both high quality and reliability of delivered energy. Acceptability is to achieve environmental and safety goals to address public acceptance. Energy savings technologies come under the third factor where they aim for the environmental and public safety towards the mitigation of global warming. Improving the energy efficiency and enhancing energy savings technology in the sector of transportation, industrial processes and so on, could lead to the reduction in the usage of fossil fuel, and this will then result in the decrease in the amount of anthropogenic CO_2. For instance, in Japan, the Japanese industries have been making efforts to gain energy by improving energy efficiency of end use technologies such as direct heating, boiler and motive power [99]. Meanwhile, in Spain, M.L. Feijoó et al. have studied the issue on the global warming and the energy efficiency of Spanish industriesusing minimum cost input in order to calculate the demand for electricity, gas and other fuels. On this basis, they found that there was no inherent conflict between the objectives of achieving productive efficiency and reducing energy consumption. Indeed, it is possible to reduce the industrial emissions of CO_2 by up to

29.4% by means of a bottom-up energy efficiency policy. However, if the government wants firms to reduce their emissions even further, then it would be necessary to implement some energy regulatory policies [101].

1.4.2 Less carbon intensive fossil fuels

According to the IPCC report, switching from high-carbon to low-carbon fuels can be very effective in reducing the CO_2 emission where suitable energy sources are available. It was estimated that about 420 kg CO_2/MWh or 50% of emission reduction can be achieved by changing from coal to gas in electricity generation [102]. Moreover, study of the CO_2 emissions from various power plants in Japan using Life Cycle Assessment (LCA) method conducted by Central Research Institute of Electric Power Industry (CRIEPI) revealed that the CO_2 emission can be reduced by about 367~456 kg CO_2/MWh or about 38%~47% in case that the liquid natural gas (LNG) is used instead of coal in the electrical power generation [103].

1.4.3 Carbon-less or carbon-free energy source and renewable energy

As mentioned above, fossil fuels are still the primary source of the world energy demand. In the current energy system, the remaining energy sources only account for about 15% of the energy needs. The use of other energy sources; wind, solar, biomass, water and so on, could lead the limitation of CO_2 emission. For example, the use of hydraulic power can reduce the CO_2 emission by about 922 kg CO_2/MWh or 95% in comparison to the coal power [103]. A lot of researches have been carried out in dealing with the development of carbon-less and renewable energy sources [104-107]. In Denmark, nearly 20% of its electricity is generated with wind power. Three-fourths of the Denmark's wind generation is produced by wind turbines owned and operated by individuals or small cooperatives that generate electricity for their own needs and sell the excess to the local users [108]. One of the reports by International Energy Agency (IEA) stated that small, stand-alone renewable energy technologies can supply electricity necessary for rural communities cheaply and have the potential to displace costly diesel-based power generation options [109]. However, in general, many of the renewable energy sources are still facing constraints related to cost, supply, land use and other environmental factor. For example, in the case of wind power, a serious obstacle against the use of wind mill is public opposition that reflecting concern over the scenery, the noise of wind turbines, and the environment for wild life. One of the most misunderstood aspects of wind power is the space for windmill. Most studies assume that wind mill occupied much

space and the mills must be spaced a wide distance between each others. This might misleads us when we try to adopt wind power generation. According to one widely circulated report in 1975, 18,000 square miles windy areas or an area about 7% the size of Texas would be required for generating 20% of US electricity from wind power [110].

1.4.4 New policies and legislations

Most of CO_2 emission mitigation techniques would not successfully achieve their target without the supports through the implementation of new policies and legislations from the regional governments and international organization. Numerous new policies and legislations have been introduced in fighting with the global warming [111-115]. The Japanese government, through their late Prime Minister Aso Taro has made an announcement regarding Japan's subsidy for Environmental Friendly Vehicles ("eco-cars") on 10th April 2009. This Japanese "eco-cars" program which is under the accelerated vehicle retirement (AVR) program was started from April 2009 till September 2010. This subsidy aimed at encouraging the purchase of fuel-efficient vehicles for the purpose of protecting the environment as well as stimulating the economy [116]. In the first period of this program, sales of U.S. and many European cars were not permitted because only vehicles complied with Japan's "Type Approval" process were qualified. Later, after a protest by the U.S. Trade Representative, the Japanese government modified the program so that certain U.S. and European vehicles would be qualified [117]. Under the subsidy program, purchasers of gas-electric hybrids and other green cars will receive up to 250,000 yen when they purchase the "eco-car", and at the same time, the purchaser must disposed their older car. The Japanese government has allocated about 583.7 billion yen for the purpose and almost all of the amounts were dried up in the early of September 2010. Such of these schemes and policies have brought a significant effect on the mitigation of the CO_2 emissions into the atmosphere. Moreover, awareness about the environmental issues could also be improved through the actions like these.

1.4.5 Carbon capture and storage (CCS)

The mitigation options that were described from 1.4.1 to 1.4.4 mostly emphasized more on the reduction of CO_2 emission from the source, than on the reduction of CO_2 concentration emitted to the atmosphere. The application of such methods might lead to the less amount of CO_2 emission to the atmosphere. However, the problem of the high concentration of CO_2 gas in the atmosphere still exists. In order to cope with this issue, application of carbon capture and storage (CCS) technology may be the right selection. The CCS technology involves

capturing the CO_2 from the preparation of fossil fuels as well as the combustion of fossil fuels, as in power generation, or. The CCS can also be applied to various processes with high amount of CO_2 emitted [18]. The major components of a CCS process include separation of CO_2 from the exhausted gas, compression of CO_2 by high pressure, transportation of CO2 from plant to stock yard and storage [118]. CO_2 storage, even with small amount of CO_2, would make an useful contribution to lowering emissions. In recent years, the technical literature on this field has expanded rapidly.

Table 1-2 Estimated potential of CO_2 storage and utilization options [131].

Option	Estimated global capacity [GtC]
Mineral CO_2 sequestration	Very large (more than the total release of oxidation of global fossil fuel reservoirs)
Ocean disposal	>1,000*
Saline aquifers [121]	27-2,700
Depleted gas reservoirs	>140
Depleted oil reservoirs	>40
Improved forestry and reforestation	50-100
Enhanced oil recovery	65
Bio fixation	1.35
Chemicals	0.09

* Without adding alkalinity the maximum capacity in oceans is limited to about 300-600 GtC [132].

There are several techniques of the CCS. These are biological storage (photosynthesis, soil carbon stock, ocean life storage etc), geological storage (underground or underwater), oil and gas reservoirs, enhanced oil recovery, chemicals fixation, membrane flash process, artificial weathering, mineral carbonation and so on [119-130]. The utilization options of CCS technologies and their estimated potential of CO_2 storage are shown in Table 1-2 [131]. The main concern of these techniques, besides applicability of them, is the temporary storage capability. CO_2 stored in the ocean, for example, will return to the atmosphere in about hundreds to thousands of years. Although it has been pointed out that the storage is not necessarily be permanent [133], the question remains as to whether re-emission of CO_2

influences future generation. Other disadvantages of ocean storage are the (local) change of pH of the water and its induced effects on the environment.

Another storage technology is the saline aquifer storage [119, 121, 134]. The worldwide CO_2 storage capacity of deep saline aquifers has been estimated to range from 100 to 10,000 $GtCO_2$ [121]. Even though there is large potential capacity, a major obstacle to it is the safety and environmental protection. Verification of long-term CO_2 residence in receptor formations and quantification of possible CO_2 leaks are required for proper assessment of environmental and public risk [135]. On the other hand, storage of large amounts of non-converted concentrated CO_2 as in oil and gas reservoirs needs continuous monitoring for an infinite time. Apart from that, accidental release of CO_2 causes major health risks, as the Lake Nyos accident in 1987 proved [136]. Enhancement of the storage capacity by additional agriculture and reforestation activities are also one of the options, but they would also be limited by land use practice, and the storage by this method might not be permanent [137]. Therefore, an alternative technology to store carbon dioxide permanently, safely and massively is CO_2 sequestration by mineral carbonation.

Mineral carbonation is based on the reaction of CO_2 with materials bearing metal oxide to form carbonates, with calcium and magnesium are the most attractive metals. In nature, such a reaction is called silicate weathering and it involves the absorption of atmospheric CO_2 into naturally occurring silicates such as forsterite (Mg_2SiO_4) and wollastonite ($CaSiO_3$). This technique was originally proposed by W. Seifritz in 1990 [138], followed by H.E. Dunsmore and Lackner et al. [13, 92]. Given the dominance of the lithosphere and the fact that the greater part of the carbon in the lithosphere is held in its oxidized form (Table 1-1), an enormous potential for carbon sequestration in solid carbonated form can be expected [13].

Mineral carbonation is attracted much attention due to some advantages. The main advantages of CO_2 sequestration by mineral carbonation are:

1. Long Term Stability - Mineral carbonation is a natural process that is known to produce environmentally safe and stable material over geological time frames. The formation of mineral carbonates insures a permanent fixation of CO_2 rather than temporary storage of the CO_2. Thereby, the mineral carbonation can guarantee no harmful legacy issues for future generations.
2. Vast Capacity - Raw materials for the mineral carbonation exist in vast quantities across the globe. The quantity of the accessible materials far exceed even the most optimistic estimate of coal reserves ($\sim 10{,}000 \times 10^9$ tons).

3. Economically Viable Potential- The overall process is exothermic and, hence, has the potential to be economically viable. In addition, its potential to produce value-added by-products during the carbonation process may compensate its costs further.

In using the mineral carbonation technique, there are several potential materials that can be used as a sorbent. These materials are classified into minerals and waste materials. In the case of minerals, there are several types of silicate rocks are available, for example wollastonite, serpentine and olivine. In the case of waste materials, alkaline industrial residues, namely slag and dust from iron and steelmaking production, fly ash and so on can be a feedstock for the mineral carbonation process [88-91, 139-143]. In the case of naturally existed material which is the silicate rocks, carbonation can be carried out either ex-situ or in-situ. The ex-situ process is performed in a chemical processing plant after mining and pre-treating the silicates, as in Fig. 1-5 [18]. On the other hand, the in-situ is carried out by injecting CO_2 in silicate-rich geological layers or in alkaline aquifers. However, even though the silicate rocks are abundantly available, generally they are difficult to be accessed. On the other hand, the quantity of the industrial residues is not as much as the silicate rocks but they are easily available and most often produced near to the emission source of CO_2. Industrial residues can also be carbonated in the same plant where they are produced.

The utilization of the industrial residue, such as steel slag, for the mineral carbonation is expected to contribute not only to the mitigation of CO_2 concentration in atmosphere, but also to the effective reutilization of unused steel slag. In the carbonation process of steel slag, gaseous CO_2 from emissions sources would be absorbed into the slag. The presence of CaO and MgO in the steel slag is expected for them to have the high potential of reaction between the slag and CO_2 as shown by the following reaction:

$$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)} \quad (1.1)$$

$$MgO_{(s)} + CO_{2(g)} \rightarrow MgCO_{3(s)} \quad (1.2)$$

The carbonation reaction is exothermic and can theoretically yield energy. However, the kinetics of natural mineral carbonation is slow; hence all currently implemented processes require energy intensive preparation of the solid reactants to achieve affordable conversion rates and/or additives that must be regenerated and recycled using external energy sources.

There are numerous methods have been applied for the mineral carbonation, i.e. natural carbonation, aqueous carbonation, heat and pressure treatment and the mechanical activation.

In the natural carbonation process, the material that acts as a sorbent will be exposed to the CO_2 without any additional treatment for the reaction to take place. However, the natural direct gas-solid reaction is too slow and thus, not suitable for the efficient CO_2 sequestration. Aqueous carbonation process is the process that using strong or weak acid, basic aqueous solutions or chelating agents to dissolve metal oxides, then react it with gaseous CO_2 which finally would lead to the production of carbonates. S. Eloneva et al. [12] has studied on the suitability of carbonation route by using acetic acid and NaOH to produce carbonates from blast furnace slag at temperature 30-70°C and pressures of 1-30 bar. From the preliminary process calculations, they found that absorption capacity of about 0.23 kg CO_2/kg slag could be achieved by the proposed carbonation process. However, the electricity required for NaOH regeneration would make the process unsuitable for CO_2 sequestration. G.M. Hernandezet al. has investigated aqueous carbonation of fly-ash from coal combustion in a stirred reactor [140]. This experimental study demonstrates that 1 ton of fly-ash could fix up to 26 kg of CO_2, i.e. 38.18 ton of fly-ash per ton of CO_2 fixed. However, this method seemed to be effective only if the very fine powders are used. Another major obstacle for the utilization of the aqueous carbonation method is the difficulty of the catalyst recovery, i.e HCl, CH_3COOH and NaOH, after the carbonation process. Furthermore, aqueous carbonation method consists of quite complicated system which resulted to the increase in the sequestration cost of CO_2.

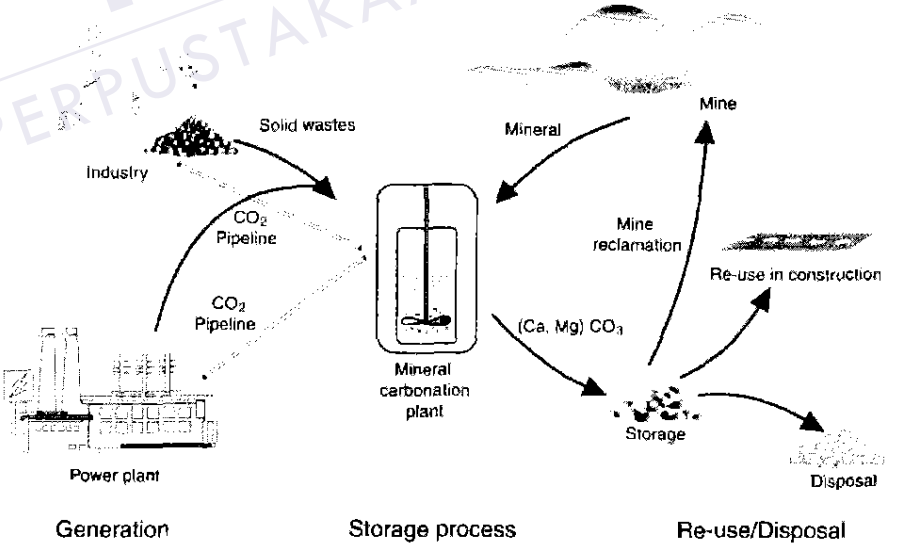


Fig. 1-5 Material fluxes and process steps associated with the ex-situ mineral carbonation of silicate rocks or industrial residues.

In the work by Huijgen et al. , a maximum carbonation degree reached 74% of the Ca content in the condition of 30 min, 19 bar pressure, 100°C, and a particle size of <38μm [13]. Baciocchi et al. [15] achieved a maximum CO_2 uptake of 0.13 kg CO_2/kg residues for the finest grain size and found that temperature was the parameter that most influenced CO_2 uptake. However, the use of high temperature and high pressure in the proposed methods seemed to contribute to the high energy penalty.

In this research, the EAF slag is mainly used as a material for the carbonation process. The EAF slag is an industrial residue that was discharged from steelmaking industry. The mechanical grinding method was applied to accelerate the carbonation process. This method has been widely used not only for the pulverization but also for the enhancement of chemical reaction such as synthesizing of nanoparticles [19, 20]. The reasons why we chose this method are because of the equipment for the grinding is relatively simple and inexpensive. It also requires neither high temperatures nor high pressures, thus low in energy consumption. Furthermore, the process itself is also simple, especially if it is not necessary to produce and separate pure products [21].

1.5 Research Objective

Our research is focusing on the one of the techniques in CCS technology which is the mineral carbonation via the utilization of dry and wet grinding method. The final objective of this research is to develop a new mineral carbonation process that have a high efficiency in the permanent absorption of CO_2 with low energy consumption and at the same time have some value added features that will finally lead to the feasibility of the overall carbonation system economically. The successfulness of the method proposed is expected to contribute to the:

1. Reduction of CO_2 gas emitted into the atmosphere.
2. New economically feasible re-utilization method of the slag.
3. Cost reduction for slag landfilling and stockpiling; more than JPY10,000/t_{slag} required
4. Prevention of the dissolution of hazardous materials from the slag into the soils during landfilling or stockpiling.

In order to achieve this target, there are several guiding questions to be highlighted in this study:

Q1-What is the appropriate grinding device and method for the process?

Q2-What kind of phenomenon occurred during the grinding; CO_2 absorption or decomposition?

Q3-What is the effect of grinding parameters on the behavior of CO_2 absorption?

Q4-What is the effect of the chemical composition and crystal structure on the behavior of CO_2 absorption?

Q5-What is the effect of dissolution of metal element into water on the behavior of CO_2 absorption?

Q6-What is the mechanism of absorption for both dry and wet grinding method?

Q7-Is the CO_2 permanently stored inside the samples?

Q8-Can the amount and the rate of CO_2 absorption be enhanced by any other additional conditions?

Q9-How much is the sequestration capacity of this method and how much can it contributes to the reduction of CO_2 gas emission from steel industry?

Q10-Can the process meets the energy requirement?

Q11-Is the process cost effective?

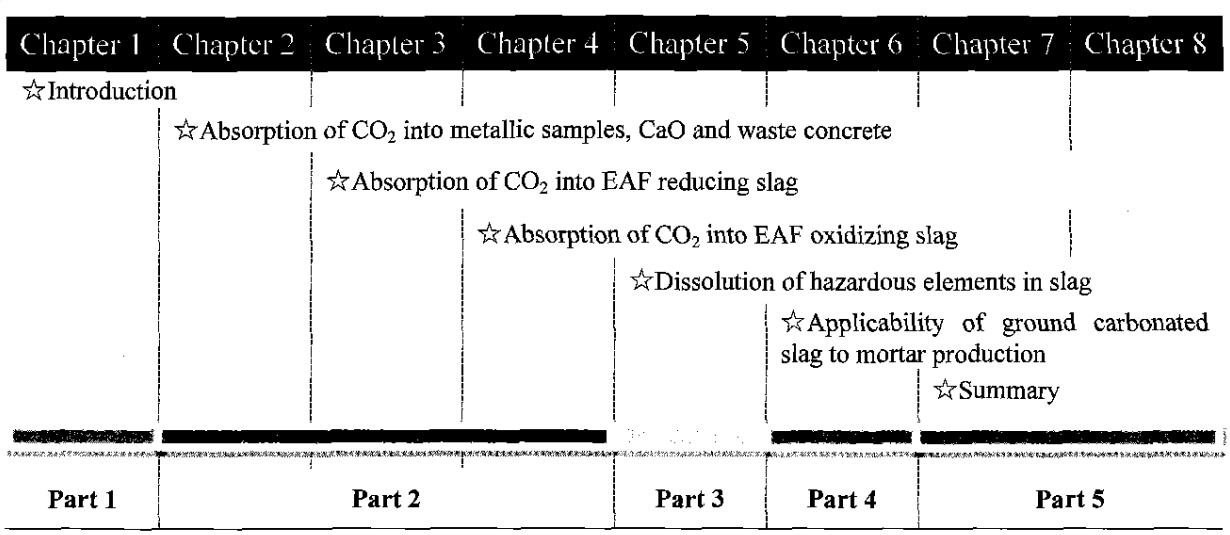
Q12-Do this process will be better than any other methods?

Q13-What is going to be done with the ground carbonated samples?

Thus, each chapter in this thesis is going to discuss and answer all the guiding questions.

1.6 Outline of this work

Table 1-2 Overview of the thesis outline



The overall outline of this thesis is as shown in Table 1-2. It consists of 5 main parts. In the first part which is the **Chapter 1**, the introduction of this work is made by explaining the background of the research, the effects of the climate change that was brought by the increase in the concentration of anthropogenic CO_2 in atmosphere, the introduction of type of slag, the introduction of the related works and finally the objective of this study.

The second part which is the investigation on the behavior of CO_2 absorption was performed in three different chapters. It involves the chapter 2, 3 and 4. **Chapter 2** is to investigate the fundamental behavior and mechanism of CO_2 absorption into metallic samples and CaO contained materials with dry grinding method in a centrifugal ball mill. The behavior of CO_2 absorption with different grinding parameters had been examined and the observation of the morphological and crystal structures with changing grinding time were carried out using SEM and XRD. The analysis of the gas remained in the grinding vessel after the grinding finished was conducted to deeply understand the mechanism of the CO_2 absorption with this method. The relationship between the amount of CO_2 absorption and the specific surface area of the ground samples was also investigated. Finally, the thermodynamic data of each metallic samples was used to investigate the relationship between the standard free energy of formation of each metal oxides and the amount of CO_2 absorption.

Chapter 3 deals with the behavior of CO_2 absorption into EAF normal and stainless steelmaking reducing slag under wet grinding in vibrating ball mill. Reaction between the slag and CO_2 during the grinding was observed by constant pressure method. The influence of each grinding parameters on the behavior of CO_2 absorption was examined. Analyses on the solid, liquid and gas sediment were conducted by SEM, EDX, XRD, ICP-AES and gas chromatography. Analysis of H_2S gas that can't be detected by gas chromatography was done by the precision gas-detector tube (Kitagawa 120SF). The change of temperature inside the grinding vessel with grinding time was also recorded to examine the influence of the changing temperature on the behavior of CO_2 absorption. The comparison of CO_2 absorption in the case of dry and wet grinding method as well as in the case of centrifugal mill and vibrating mill were performed. Finally, the potential capacities of CO_2 absorption for each sample were calculated.

Chapter 4 discussed profoundly about the behavior and mechanism of CO_2 absorption into EAF normal and stainless steelmaking oxidizing slag under wet grinding by vibrating ball mill. The experiments conducted were similar to that in the case of EAF reducing slag described in chapter three. The comparison of CO_2 absorption behavior for all samples was made and the effect of the chemical composition and the crystal structure on the behavior of

CO_2 absorption was clearly explained. ICP-AES was used to perform the analysis on the dissolved concentration of metal elements in the slag into water and the analysis data was then used to investigate the influence of the dissolved concentration on the absorption of CO_2. Relations between the dissolution of element and pH theoretically and experimentally were also shown. The power consumption by the vibrating mill during the process was measured and the evaluation on the amount of CO_2 gas that was emitted during power generation to supply electrical power to the apparatus was performed using life cycle assessment (LCA) CO_2 data. Overall comparison between the CO_2 absorption and CO_2 emission for each sample was also included in this chapter. Finally, comparison of the absorption potential between this method and other methods was also made.

The third part which is the investigation on the extraction behaviors of environmentally regulated substances which are zinc and chromium were performed in the **Chapter 5**. The influences of each grinding parameters; type of slag, type of grinding media, partial pressure of CO_2 and atmosphere of the grinding vessel, on the extraction behavior were also investigated. Leaching of the ground slag into the aqueous solution was also performed. ICP-AES was mainly used to investigate the dissolution behavior of each element into water.

Fourth part is about the application of the ground slag as a material for the concrete mortar. This was discussed in the **Chapter 6**. The preparation of mortar, the flow test and the compressive test was performed based on the JIS A6206-1997 (Ground granulated blast-furnace slag for concrete). This regulation contains some of the matter of the JIS R 5201-1997 (Physical testing method for cement). The extraction capability that might be observed in chapter five and the usability of the ground carbonated slag as a material for cement in chapter six would be the value added for utilizing this method.

In the last part which is the **Chapter 7**, the summary of all results obtained was made.

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